

The Kinetics of Aromatic Nitration

Ameya P. Diwan, Sanjay M. Mahajani, and Vinay A. Juvekar*

Abstract—**Nitration reactions are generally conducted using mixed acid. These are extremely exothermic, and tend to run away. Our study show that the reaction is more complex than it is generally believed. We have provided some preliminary evidence to show that nitrobenzene, above a critical concentration of sulfuric acid exists forms microemulsion at ambient temperatures. This hypothesis is consent with anomalous solubility of nitro-aromatics in concentrated sulfuric acid. There is also formation of Winsor III-phases. In this work we have studied kinetics of nitration of nitrobenzene (NB) (below solubility limits) in concentrated sulfuric acid (> 82% w/w) and found that although the reaction follows second order kinetics, the rate constant show a discontinuous decrease after a critical loading of the organic phase. Reaction is also inhibited by addition of dinitrobenzene (DNB). We have provided the explanation for this finding based on the hypothesis that the reaction between nitrobenzene and nitronium ions occurs on the surface nitrobenzene micelles which are stabilized by concentrated sulfuric acid. This phenomenon is likely being responsible for causing runaway condition in the nitrator.**

Index Terms— Interfacial Science, Microemulsion, Nitroaromatics, Nitration, Reaction kinetics.

I. INTRODUCTION

Nitration is considered as one of the most hazardous industrial processes because it is highly exothermic and tends to be runaway. From the safety consideration point of view most polynitration reactions are conducted in a series of small reactors operated in a batch mode. These reactors are operated from remote location. The origin of the explosive nature of nitration reaction lies in the peculiar behavior of the reaction and this work is an attempt made to bring out some of the peculiarities of this reaction using nitration of nitrobenzene as model reaction. We have suggested a mechanism which explains these peculiarities. We think that this study can provide clues to the hazardous nature of the nitration reaction.

A. P. Diwan is with Department of Chemical Engg. Indian Institute of Technology Bombay, Mumbai, MH 400076 India. (e-mail: ameyadiwan@iitb.ac.in).

S. M. Mahajani is with Department of Chemical Engg. Indian Institute of Technology Bombay, Mumbai, MH 400076 India (e-mail: sanjaym@iitb.ac.in).

V. A. Juvekar is with Department of Chemical Engg. Indian Institute of Technology Bombay, MH 400076 India (phone: +91-22-2576-7236; fax: +91-22-25726895; e-mail: vaj@iitb.ac.in).

Our hypothesis is that nitrobenzene forms microemulsion above a critical concentration of sulfuric acid (> ca 80% w/w) and the critical loading of nitrobenzene. Nitrobenzene is a polar molecule and in the presence of concentrated sulfuric acid, its polarity may get enhance due to the association of the nitro-group with hydrogen ions. It is therefore likely that beyond a critical concentration of the acid, nitrobenzene tends to aggregate with nitro-group exposed to sulfuric acid and aromatic groups shield from the acid. The important evidence for this hypothesis is the sudden increase in the solubility nitrobenzene in sulfuric acid beyond 80% w/w concentration. We also show below the existence of Winsor three phases in nitrobenzene-sulfuric acid-water system. Further evidence is based on kinetics of nitration of nitrobenzene, as discussed below.

Based on the present hypothesis, the reaction between nitrobenzene and nitronium ions occurs mainly on the interface of the nitrobenzene microphase and sulfuric acid. Nitrobenzene is thus shielded from the attack on the nitronium ions. Thus it provides a natural control on the rate of nitration. The microemulsion is very stable over a certain range of temperature. At a critical temperature called inversion temperature, microemulsion phase unstable and a homogeneous solution results. At this point, the reaction between nitroaromatic species and nitric acid may increase to a catastrophic level. For better control of the polynitration reactions, it is necessary to understand their behavior in the vicinity of the inversion point.

II. EXPERIMENTAL SECTION

The experiments on nitration of nitrobenzene are conducted in a batch reactor (working volume of 0.1 L). Nitrobenzene is used as the model reactant for mixed acid (H_2SO_4 & HNO_3) nitration. Reactions are conducted under isothermal condition, in a jacketed batch reactor with stirring system (1000±100 RPM). Reactor is used at a relatively lower concentration of sulfuric acid (81-85 % w/w). The reaction mass is monitored at regular intervals of time, by quenching the sample with chilled methanol-water mixture (so that the reaction is suppressed) and analyzed for conversion of nitrobenzene and the product distribution using HPLC. The reaction is studied with respect to strength of sulfuric acid, concentration of nitric acid, mole ratio of nitrobenzene and nitric acid. All reactions are conducted under the single phase condition.

Few phase equilibrium experiments were also performed under nonreacting conditions (i.e. in the absence of nitric acid) to identify formation of three distinct phases supporting the hypothesis of formation of microemulsions.

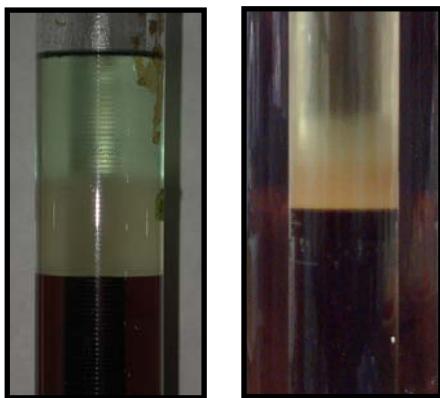


Fig.1: Winsor-III phase formation in NB-H₂SO₄-water system.

Table I: Three phase composition (at 26 °C, 1 atm)

Components	Initial Composition (% w/w)	Final Composition (% w/w)		
		Top Phase	Middle Phase	Bottom Phase
Sulfuric acid	84.93	0.99	61.94	78.27
Water	15.07	0.09	0.05	21.72
Nitrobenzene	100.00	98.92	38.01	0.01

III. RESULTS AND DISCUSSION

A. Formation of Winsor-III Phases

Fig.1 shows the Winsor-III phase formation in the system NB-H₂SO₄-water. The analysis of the three phases is also reported in the Table I. The middle phase is the microemulsion phase, whereas the top and the bottom phases are respectively, the organic and the acid phase.

B. Reaction Kinetics

The reaction between nitrobenzene and nitric acid follows second order kinetics. However, the second order rate constant is seen to decrease with increase in the initial concentration of nitrobenzene as shown in Fig.2. The rate constant also decreases with increase in the initial concentration of added dinitrobenzene.

From these two figures, it is evident that the rate constant depends on organic phase loading and not on constitution of the organic phase.

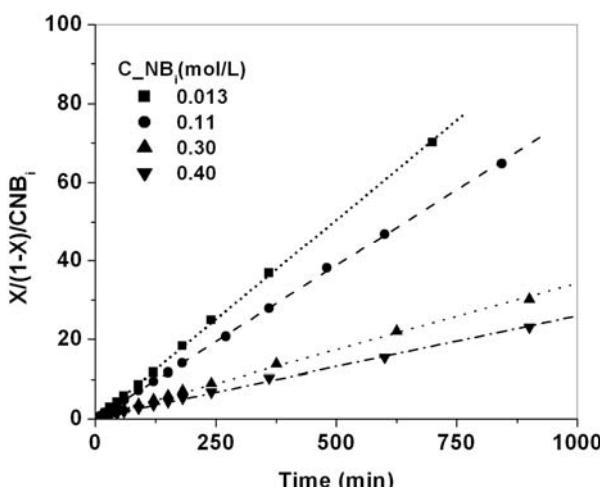


Fig.2 (a): Dependence of k_2 on the initial concentration of nitrobenzene

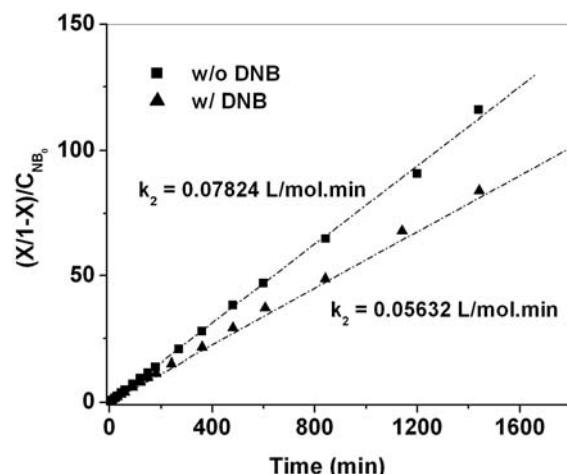


Fig.2 (b): Effect of initial loading of DNB on kinetics (H₂SO₄ – 83.35 % w/w; Equimolar reaction w.r.t. HNO₃ and NB and DNB; Temperature: 25.8 °C)

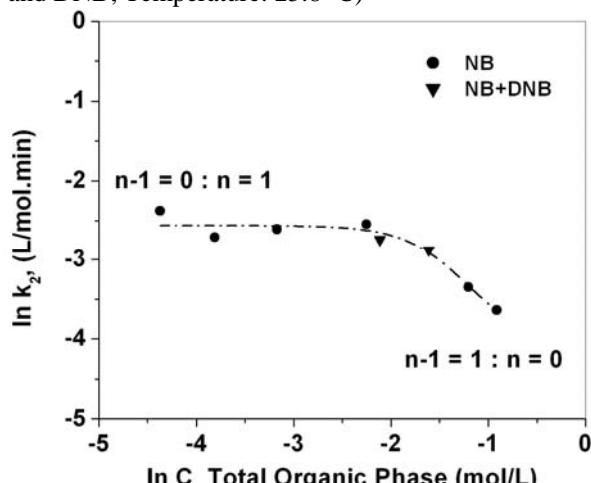


Fig.3: Model fitting for NB and DNB loading dependence. Parameters: H₂SO₄ – 83.25 % w/w, Equimolar reaction w.r.t. HNO₃ and Nitrobenzene.

This is evident from the Fig.3, in which the rate constant is plotted against total organic phase concentration. Two distinct regimes are found, with a clear break in trend at $\ln C = -2.2$ ($C = 0.1 \text{ mol/L}$).

C. Kinetic Model

A kinetic model has been proposed based on the hypothesis that nitro compounds form microemulsion at higher strength of sulfuric acid and above critical concentration of nitric acid. The nature of microemulsion is not precisely known. It could be in the form of swollen micelles, bilayers or bicontinuous forms of microemulsion. Dinitrobenzene generated during the reaction (or present in the reaction mixture in the beginning of nitration) forms a mixed microemulsion with nitrobenzene present in the system. It is assumed that the rate of the homogeneous reaction in the bulk is negligibly small compared to that of the reaction occurring in the microemulsion phase. Entire reaction is assumed to occur at the surface of the microemulsion phase.

The rate of reaction per unit volume of the total solution can therefore be expressed as

$$r_V = r_A a \quad (1)$$

where r_V is the rate of nitration per unit volume of the solution ($\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$), r_A is the rate of nitration per unit area of the interface ($\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) and a is the interfacial area per unit volume of the solution (m^{-1}). We can write, in general

$$a = n a_d \quad (2)$$

where n is the number of microphase domains per unit volume of the solution and a_d is the area of a single domain. It is assumed that the interface between the microphase and the bulk phase contains only adsorbed nitrobenzene and dinitrobenzene. Nitronium ions, which are present in the bulk solution phase, react with nitrobenzene on the surface of the microphase. We assume that the specific rate of surface reaction is proportional to the surface fraction of the microphase occupied by nitrobenzene ψ_N . i.e.

$$r_A = k_A \psi_N [\text{HNO}_3] \quad (3)$$

Nitrobenzene and dinitrobenzene will compete with each other to occupy the interface. We assume that both have same adsorption equilibrium constant. This yield the following expression for the rate of reaction

$$r_A = \frac{k_A [NB]}{[NB] + [DNB]} [\text{HNO}_3] \quad (4)$$

and the rate constant based on volume is given by

$$k_2 = \frac{k_A a}{[NB]_i + [DNB]_i} \quad (5)$$

Dependence of a on the concentration $[NB]_i + [DNB]_i$ can be expressed as

$$a = k_a ([NB]_i + [DNB]_i)^n \quad (6)$$

where n depends on the shape of the microphase. It is -1 for spherical micelles and 0 for a bicontinuous phase.

$$k_2 = k_A k_a ([NB]_i + [DNB]_i)^{n-1} \quad (7)$$

Since n is less than 1, we expect k_2 to decrease with an increase in the total organic loading. From Fig.3, we find that $n = 0$, indicating that the microemulsion is in bicontinuous form.

IV. CONCLUSIONS

The present study provides some evidence for the hypothesis that nitrobenzene forms microemulsion in high concentration of sulfuric acid. Based on the proposed model and the experimental data we find that the microemulsion is bicontinuous type. Further studies are in progress to obtain more insight into this reaction system.

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